

Processing Composite Samples from Training Ranges: Proposed Modifications to Method 8330

**Alan D. Hewitt, Marianne E. Walsh
and Thomas F. Jenkins**

**ERDC-CRREL
Hanover, NH**



**US Army Corps
of Engineers®**
Engineer Research and
Development Center

Acknowledgements

- SERDP - Bradley Smith, Dr. Jeff Marqusee and Robert Holst
- AEC - John Buck and Martin Stutz
- CHPPM - Barrett Borrey, Ken Mioduski, and Mike Brown
- EOD support teams
- Range control and base environmental personnel
- Sampling teams from ERDC, DRDC (Canada), USACHPPM, and Sacramento District Corps of Engineers

Presentation Objectives

- * Implications of <0.6 mm Vs. <2 mm sample particle size cut off
- * Processing of composite soil samples for the analysis of energetic residues

Challenge

- Obtaining “representative subsample” i.e., subsample containing **particles** in same proportions as bulk sample
 - Compositional Heterogeneity: difference in concentration between particles
 - Distributional Heterogeneity: nonrandom distribution of particles

Artillery Range - 29 Palms



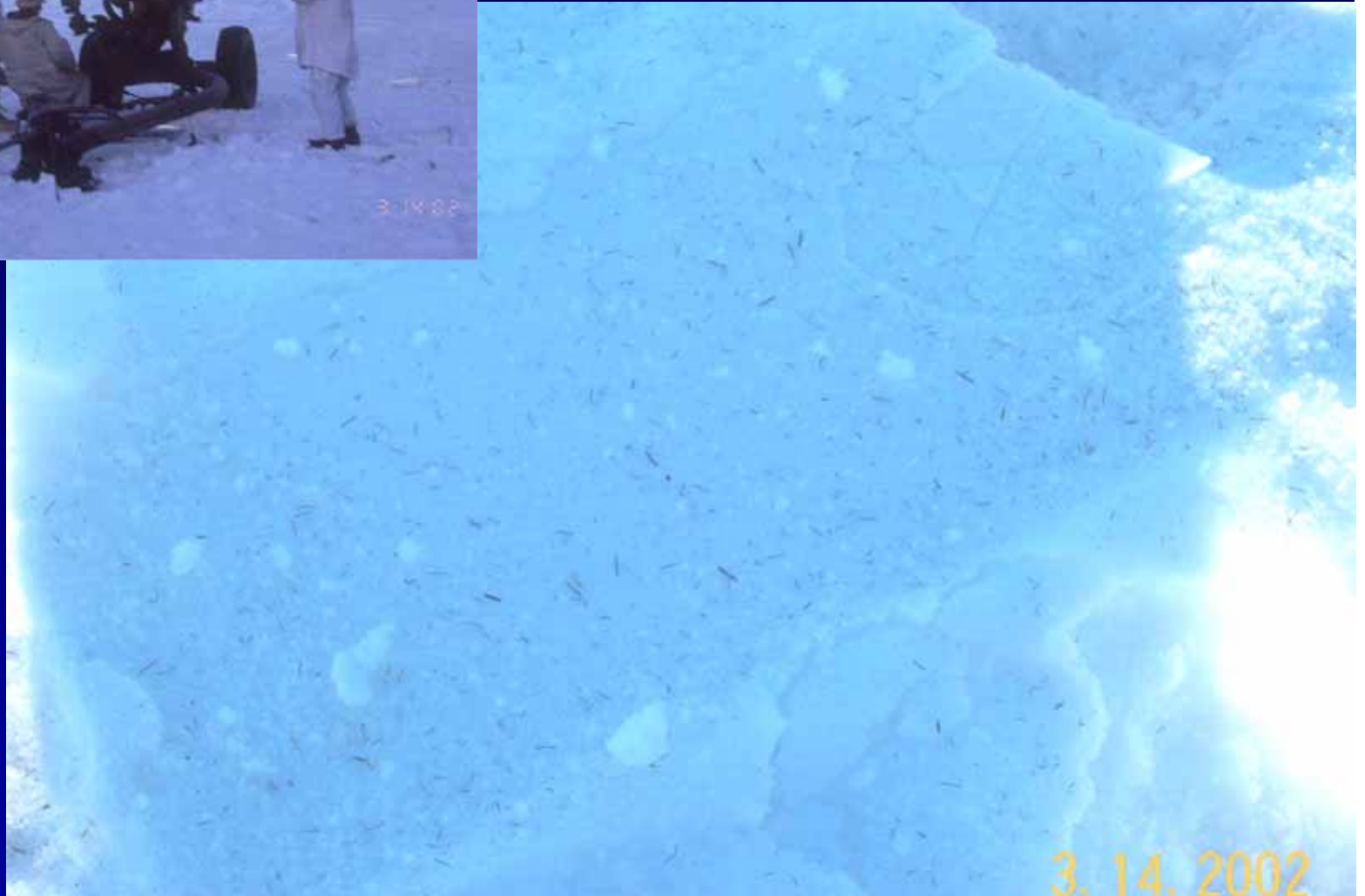
Ft. Hood: Low-order residue filled crater



Hand Grenade Low-Order Detonations: Ft. Lewis



Propellant Fibers: Ft. Richardson





Rocket Propellant: 29 Palms









Subsampling Error

- Fundamental Error: i.e., compositional heterogeneity
 - subsample size relative to contaminant particle size
- Segregation Error: i.e., distributional heterogeneity
 - non-discrimination of particles (size, shape, density)

Anticipated RSDs from Laboratory Subsampling*

Soil density 2.5 g/cm³

<u>Particle Size</u>	<u>15%</u>	<u>10%</u>	<u>5%</u>
0.5 mm	0.15 g	0.325 g	1.25 g
1 mm	1.1 g	2.5 g	10 g
2 mm	10 g	20 g	80 g

*This is an approximation. Doesn't apply if analyte of interest exist as a few discrete “**nuggets**”

Labtech Essa Ring Mill: Composite Sample Grinding

Non-vegetated 60 seconds

Vegetated 90 seconds







Subsampling

- **Evenly spread ground sample on flat surface**
- **Collect multiple (>20) increment from random locations**
- **10 g or larger subsample recommend (extracted with twice the volume of acetonitrile)**

- Subsampling error – effect of grinding on standard deviation in hand grenade range soil (50 g subsamples of < 2 mm fraction)



Subsample	TNT Conc. mg/kg		RDX Conc. mg/kg	
	Not Ground	Ground	Not Ground	Ground
1	0.25	2.03	1.68	4.75
2	1.81	2.04	1.77	4.71
3	0.37	2.00	1.46	4.80
4	1.48	2.03	3.80	4.73
5	7.93	1.97	7.83	4.67
6	0.56	2.00	1.81	4.66
7	0.35	1.90	2.35	4.62
8	0.75	2.02	2.51	4.62
9	0.56	1.97	2.08	4.64
10	0.35	1.98	1.98	4.69
11	0.62	1.90	1.68	4.66
12	5.62	1.91	13.0	4.60
mean	1.72	1.98	3.50	4.68
std dev	2.46	0.051	3.47	0.057
RSD	143%	2.57%	99%	1.23%

Comparison of Laboratory Subsample Duplicates

		<u>mg/kg</u>		
<u>Subsample</u>	<u>Analyte</u>	<u>LD-1</u>	<u>LD-2</u>	<u>RPD</u>
SC-10	NG	0.53	0.12	130%
SC-10	HMX	2.5	2.7	7.7%
SC-21	TNT	13	13	0.0%
SC-21	RDX	34	34	0.0%
SC-21	HMX	5.4	5.2	3.8%
SC-32	NG	0.28	0.35	22%
PTA-5	NG	13	13	0.0%
PTA-13	NG	0.38	0.59	43%
PTA-13	2,4-DNT	0.52	0.85	48%
PTA-22	NG	15	13	14%
PTA-29	NG	3.2	3.2	0.0%
PTA-39	2,4-DNT	0.18	0.18	0.0%

Potential Remedies (propellant residues)

- Full sample extraction
- Increase grinding period to 5 min.
(five separate 60 second grinds)



10:0

Case study: Pohakuloa Training Area & Scholfield Barracks

- **89 Split composite samples**
- **NG, 2,4-DNT, TNT, RDX, and HMX detected**
- **93 potential pairs of values above 0.2 mg/kg**
 - **Contract laboratory reported 43 values that were below 0.2 mg/kg or were qualified as “j” (46% of potential pairs)**
 - **CRREL reported 1 value below 0.2 mg/kg (1.1% of potential pairs)**

Fractionation study: 105-mm Howitzer Firing Point Samples

<u>2,4-DNT mg/kg [mass-mg]</u>			
<u>Sample</u>	<u>>2 mm</u>	<u><2 to >0.6mm</u>	<u><0.6 mm</u>
A	<d [<d] *	1.9 [1.5]	0.42 [0.68]
B	<d [<d]	3.3 [1.6]	0.51 [0.60]
C	<d [<d]	1.4 [0.78]	0.50 [0.5]

* <d below PQL

Fractionation study: Ft. Hood Crater Samples

<u>Sample</u>	<u>RDX mg/kg [mass-mg]</u>		
	<u>>2 mm</u>	<u><2 to >0.6mm</u>	<u><0.6 mm</u>
Crater A	NA *	0.86 [0.13]	5.14 [0.936]
Crater B	NA	367 [29.3]	1690 [181]

* NA - Not analyzed (Chunks of explosives should be weighed)

Fractionation study: Ft. Lewis Hand Grenade Range

<u>TNT mg/kg [mass-mg]</u>			
<u>Sample</u>	<u>>2 mm</u>	<u><2 to >0.6mm</u>	<u><0.6 mm</u>
2-1	0.21 [0.04]	1.36 [0.31]	0.81 [0.65]
2-2	0.02 [0.05]	21.0 [5.10]	2.71 [1.93]
2-3	0.36 [0.07]	3.28 [0.70]	0.55 [0.39]
2-4	0.18 [0.04]	0.42 [0.10]	2.41 [1.63]
2-5	0.30 [0.05]	5.72 [1.23]	1.65 [1.19]

Recommended Changes to Method 8330: Training Range Characterization

- **Inclusion of all particles less than 2 mm**
 - 10 mesh sieve Vs. 30 mesh sieve
- **Mechanical Particle size reduction prior to subsampling (10 g subsamples)**
 - Acquisition of grinder (Ring Mill grinder \$8K)
- **Inclusion of NG**
 - Dual (or multi) wavelength detector
- **Pre-screening of sample extracts**